

Earth and Environmental Sciences

Special Topic: Frontiers of Stable Isotope Research

Carbonate-associated sulfate: New perspectives from high-dimensional isotope systematics

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Abstract: Carbonate-associated sulfate (CAS) refers to trace sulfate structurally substituted into carbonate lattices and serves as a faithful archive of ancient seawater sulfate, regulating the biogeochemical cycles of sulfur, oxygen, and carbon. High-dimensional isotopic compositions, particularly mass-independent fractionation effects, have established CAS as a premier proxy for reconstructing ancient atmospheric and oceanic conditions. Here I review the fundamentals of CAS formation and preservation, persistent analytical and interpretive challenges, and advances in applications of high-dimensional isotope systematics. I argue that integrating sequential extraction protocols with multi-isotope measurements allows for robust screening of diagenetic overprints and contamination. Methodological and conceptual developments have propelled CAS research through three critical transitions: from isolated data points to continuous chemostratigraphic records; from single-proxy reliance to integrated multi-isotope frameworks; and from qualitative interpretations toward rigorous, quantitatively constrained models. By synthesizing high-dimensional isotopic data with biogeochemical modeling and complementary geochemical proxies, CAS emerges as a powerful tool for deciphering Earth's oxygenation history, atmosphere-ocean redox feedbacks, and the co-evolution of life and planetary habitability.

Keywords: carbonate-associated sulfate, high-dimensional isotope, triple oxygen isotope, Earth oxygenation history, biogeochemical cycle

INTRODUCTION

Sulfate (SO_4^{2-}) is one of the most abundant oxidized anions in Earth's surface environments and constitutes a central component of the global sulfur cycle [1–4]. In these environments, sulfate acts as a redox-sensitive species that links oxidative and reductive sulfur transformations, thereby coupling sulfur cycling to the broader oxygen redox budget [5–10]. Under oxic conditions, molecular oxygen produced by oxygenic photosynthesis drives the oxidation of reduced sulfur species, including hydrogen sulfide, elemental sulfur, and organic sulfur compounds, leading to the accumulation of sulfate [6,11,12]. Conversely, in anoxic environments, sulfate serves as a terminal electron acceptor during microbial sulfate reduction, coupling the

oxidation of organic matter to the production of reduced sulfur species and dissolved inorganic carbon (HCO_3^-) [13]. The resulting bicarbonate is commonly preserved as authigenic carbonate minerals, while reduced sulfur is ultimately sequestered as pyrite in sediments [7,14,15]. Through these complementary processes, sulfate mediates the transfer of redox equivalents between the carbon and oxygen cycles, exerting a fundamental control on Earth's surface redox balance [16]. This central geochemical role underpins its value as a tracer of redox conditions and biogeochemical evolution in Earth's surface environments [17–22].

Sulfur has four stable isotopes (^{32}S , ^{33}S , ^{34}S , and ^{36}S), while oxygen has three (^{16}O , ^{17}O , and ^{18}O), providing the fundamental basis for recording their diverse isotopic fractionation processes in Earth's surface [6,7,22]. Beyond conventional mass-dependent fractionation, both isotope systems also exhibit mass-independent fractionation, enabling sulfate to preserve high-dimensional isotopic information that reflects complex redox and photochemical processes [22,23]. As a result, sulfate encodes multiple and high-dimensional isotopic signals, including: (1) the triple-oxygen-isotope system ($\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$); (2) the quadruple-sulfur-isotope system ($\Delta^{33}\text{S}$, $\Delta^{36}\text{S}$, and $\delta^{34}\text{S}$); (3) coupled sulfur-oxygen isotope relationships ($\delta^{34}\text{S}$ versus $\delta^{18}\text{O}$); and (4) clumped isotopes, which involve rare multi-isotope substitutions such as $\Delta^{34}\text{S}^{18}\text{O}$ [24]. Capital delta (Δ) notation is used to quantify deviations of measured isotopic compositions from a reference mass-fractionation line. For oxygen isotopes, $\Delta^{17}\text{O}$ is defined as $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.5305 \times \delta^{18}\text{O}$, where $\delta' \equiv \ln(R_{\text{sample}}/R_{\text{reference}})$ and R denotes the molar ratio $^{17}\text{O}/^{16}\text{O}$ or $^{18}\text{O}/^{16}\text{O}$. This formulation expresses the deviation of $\Delta^{17}\text{O}$ from its expected value based on $\delta^{18}\text{O}$ (i.e., $\Delta^{17}\text{O} = \theta \times \delta^{18}\text{O}$, with $\theta = \ln^{17}\alpha/\ln^{18}\alpha$) [25]. Analogously, sulfur MIF is expressed as $\Delta^{33}\text{S} = \delta^{33}\text{S} - 0.515 \times \delta^{34}\text{S}$ and $\Delta^{36}\text{S} = \delta^{36}\text{S} - 1.9 \times \delta^{34}\text{S}$ [26,27]. These high-dimensional isotopic signatures of sulfate are essential tools for identifying sulfate sources, studying the rates, pathways, and reservoir changes in sulfur and oxygen cycles, and reconstructing ancient atmospheric and oceanic environments [28–32].

Ideally, sulfate-bearing minerals such as gypsum and barite provide the most direct records of marine sulfate isotopic compositions [33–38]. However, these minerals are often discontinuously deposited, restricted to specific depositional settings (e.g., shallow or evaporitic environments), and susceptible to post-depositional alteration and fluid overprinting, limiting their temporal coverage and complicating integration with other geochemical proxies [16,39–41]. In contrast, trace sulfate incorporated into carbonate crystal lattices offers a more continuous and stratigraphically coherent archive [42]. Because carbonates are widespread in marine successions and commonly preserve multiple geochemical signals, CAS enables the reconstruction of seawater sulfate compositions alongside other isotopic and elemental proxies, providing robust insights into past ocean chemistry and surface redox conditions [43–48].

As early as the 1960s, trace sulfate ions were detected in both recent and ancient sedimentary carbonates [49]. However, the form of sulfate in carbonates was not confirmed until 1984, when Takano [50] used laser Raman and infrared spectroscopic methods to verify the presence of sulfate ions in both biogenic and marine inorganic carbonates, hypothesizing substitution within carbonate lattices. Pingitore Jr. *et al.* (1995) [51] confirmed via K-edge X-ray absorption near-edge structure (XANES) that sulfate is not present as gypsum or anhydrite inclusions but substitutes for carbonate ions. Sulfur is present as sulfate in various biogenic and diagenetic carbonates.

Burdett *et al.* (1989) [52] were the first to extract sulfate from foraminifera for sulfur isotope analysis, aiming to reconstruct the isotopic composition of ancient marine dissolved sulfate. They noted that sulfate exists in multiple forms, including lattice-bound ions, fluid inclusions, organic polysaccharides/proteins, and adsorbed phases, and argued that all forms could potentially record marine isotopic signatures. Consequently,

they introduced the term “carbonate-associated sulfate” (CAS). In practice, however, only sulfate ions (SO_4^{2-}) structurally substituted into carbonate mineral lattices during precipitation faithfully reflect ambient seawater sulfate [53,54]. Richardson *et al.* (2019) [55] used μ -XRF imaging and XANES spectroscopy to distinguish inorganic sulfate from sulfate esters in brachiopod shells, although organic sulfate esters occur only in trace amounts. Therefore, CAS is now defined specifically as lattice-substituted sulfate ions. The primary mechanism for CAS incorporation is isomorphic substitution. The vast majority of sulfur in carbonate minerals is tetrahedral sulfate substituting for trigonal planar carbonate ions [51,56,57]. CAS concentrations range from tens to thousands of parts per million (ppm) in modern marine carbonates, often lower in ancient rocks due to diagenetic loss [58]. These concentrations depend on mineralogy, the dissolved $\text{SO}_4^{2-}/\text{CO}_3^{2-}$ activity ratio, precipitation rate, and diagenetic processes [59–62].

Barkan *et al.* (2020) [63] conducted carbonate precipitation experiments to quantify CAS sulfur isotope fractionation in both calcite and aragonite, examining its dependence on precipitation rate and aqueous sulfate concentration. In aragonite, the fractionation is $1.0\text{‰} \pm 0.3\text{‰}$ and appears independent of sulfate concentration. In calcite, fractionation covaries strongly with sulfate concentration and weakly with precipitation rate, ranging from $1.3\text{‰} \pm 0.1\text{‰}$ to $3.1\text{‰} \pm 0.6\text{‰}$. Theoretical equilibrium fractionations at 25 °C, calculated using reduced partition function ratios, are 3.6‰, 4.5‰, and 4.0‰ for calcite, aragonite, and vaterite, respectively [53,64]. To date, no studies have addressed oxygen isotope fractionation during sulfate incorporation into carbonate.

Although carbonate precipitation involves several per mil of sulfur isotope fractionation, this does not prevent the reconstruction of paleo-seawater sulfate sulfur isotopes. Since Burdett *et al.* (1989) [52], CAS in marine carbonates has been considered to faithfully record the sulfur and oxygen isotopic composition of seawater sulfate, as evidenced by hundreds of publications (Figure 1). Nevertheless, the main challenges arise from isotopic modifications during early and later diagenesis.

(1) Early diagenesis. Microbial sulfate reduction and the re-oxidation of sulfide or other reduced sulfur species (e.g., elemental sulfur, organic sulfur) continue in pore waters during early carbonate diagenesis, altering the sulfate inherited from ambient seawater. $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ of pore water sulfate typically increase due to dominant microbial sulfate reduction [7,65,66]. The deviation of CAS isotopes from primary seawater values depends on sulfate concentration, redox conditions, bioturbation degree, sediment porosity, precipitation rate, microbial sulfate reduction rate, and organic matter content [21,41,61,67].

(2) Later diagenesis. Increasing burial temperature enhances water-rock interactions. $\delta^{18}\text{O}_{\text{CAS}}$ can increase via oxygen isotope exchange between CAS and carbonate during (re)crystallization [68]. Thermochemical sulfate reduction may occur at 100–200 °C in the presence of sufficient organic matter, elevating both $\delta^{18}\text{O}_{\text{CAS}}$ and $\delta^{34}\text{S}_{\text{CAS}}$ [69]. Meteoric or other externally derived fluids can supply dissolved O_2 that oxidizes sulfide minerals, generating new sulfate and causing dissolution of primary carbonate, followed by precipitation of secondary carbonate cements [61]. Meteoric waters may also introduce dissolved sulfate from atmospheric sources or soluble sulfate minerals and salts, which can mix into secondary carbonates and contaminate primary CAS (Figure 2).

Therefore, this review begins with an overview of the extraction and analytical methods employed to systematically assess diagenetic alterations and contamination using high-dimensional isotopic data of CAS, followed by a discussion of its applications.

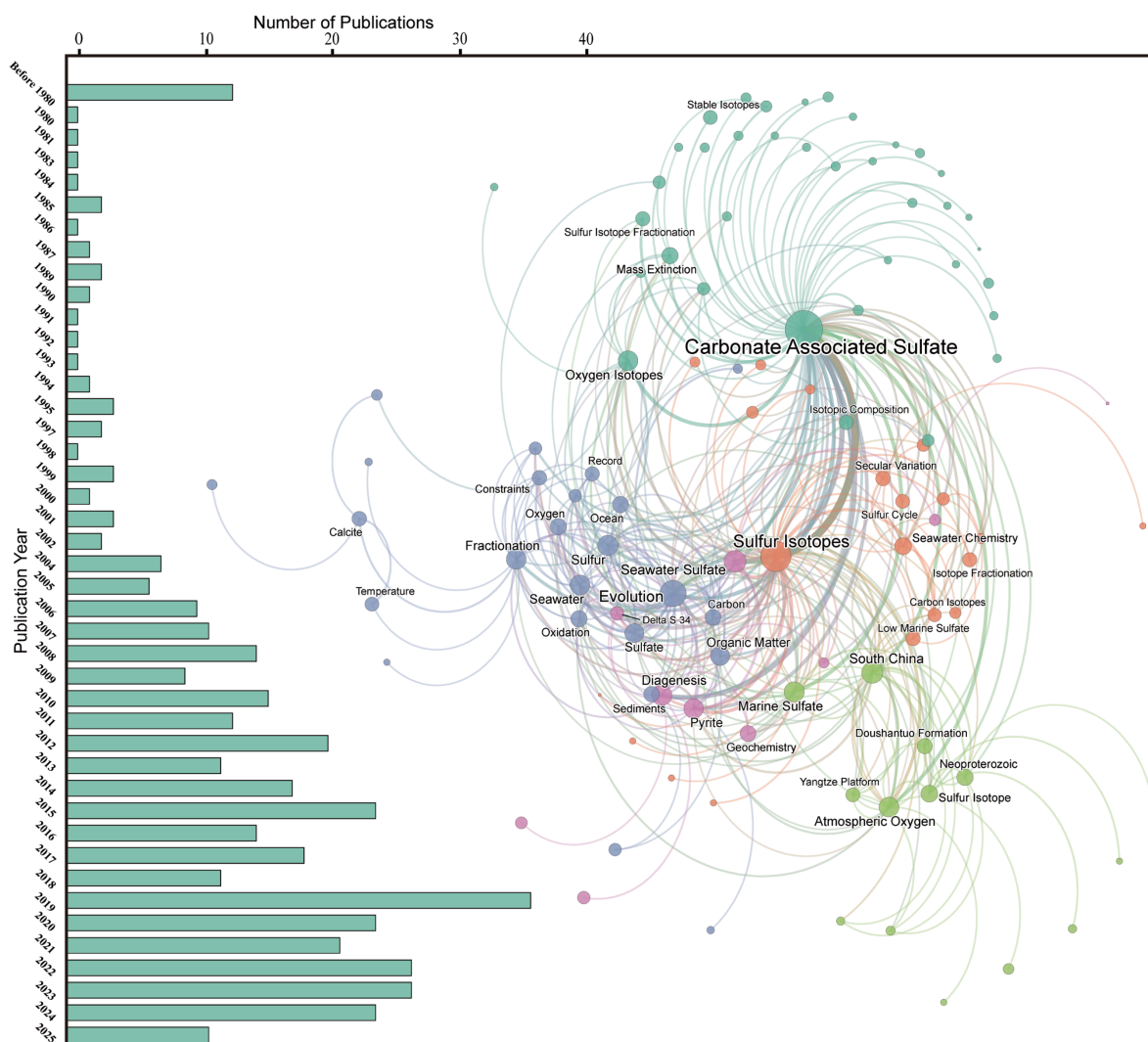


Figure 1 Co-occurrence network of research topics related to CAS. The network illustrates the relationships among frequently used keywords in CAS-related studies. Node size reflects keyword frequency, while links represent co-occurrence strength within the literature. The clustering highlights major research themes, including sulfur and oxygen isotopes, seawater sulfate, paleoenvironmental applications, and geochemical cycles.

CAS EXTRACTION AND ISOTOPE MEASUREMENT

Sulfate extraction

The standard procedure for extracting CAS from carbonate minerals involves first dissolving the carbonate matrix with hydrochloric acid (HCl) to release the sulfate ions, followed by precipitation of barium sulfate (BaSO_4) through the addition of a saturated barium chloride (BaCl_2) solution. Carbonates, however, contain multiple sulfate species, including primary CAS (lattice sulfate) and non-CAS derived from sources such as pyrite oxidation or atmospheric sulfate. As discussed in the introduction, it is therefore critical to isolate CAS from non-CAS and to remove or minimize contributions from sulfur-bearing phases—such as organic sulfur,

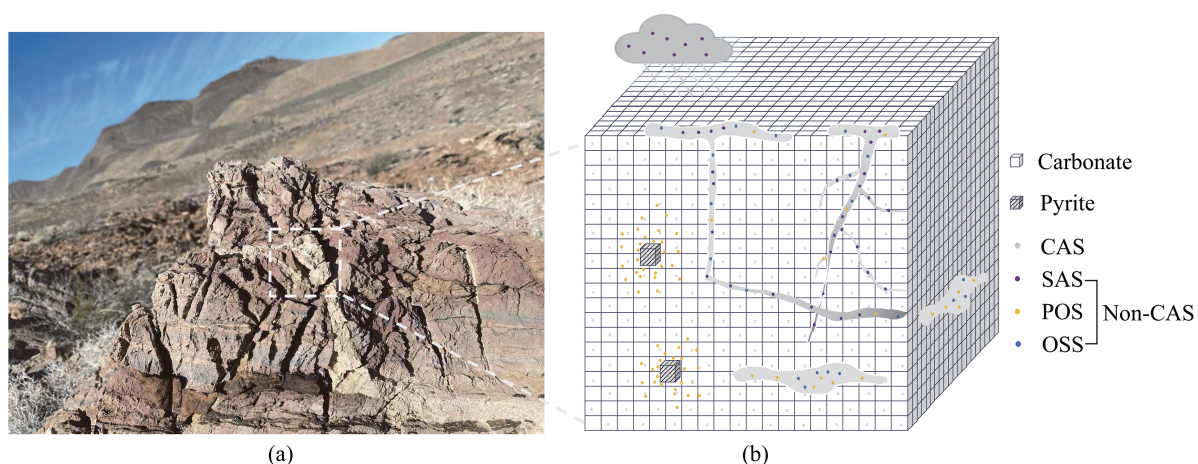


Figure 2 Schematic illustration of sulfate species in outcrop carbonate rocks. (a) Outcrop of Neoproterozoic dolostone from the Johnnie Formation, Death Valley, USA. (b) Conceptual diagram showing different sulfate species present in carbonate rocks, including CAS (lattice-bound sulfate) and non-CAS sulfate sources, comprising secondary atmospheric sulfate (SAS), pyrite-oxidation sulfate (POS), and other sulfate sources (OSS).

metastable sulfides, and acid-volatile sulfur (AVS)—that could otherwise introduce spurious sulfate during the extraction process.

A commonly employed method to remove non-CAS sulfate associated with secondary carbonate phases is leaching with a sodium chloride (NaCl) solution. This approach exploits the fact that secondary carbonate, typically present as calcite, is more readily crushed and exposed than the primary host carbonate during sample preparation. In practice, a 10% NaCl solution is widely used, based on three key properties of calcite: (1) calcite dissolves more rapidly in high-concentration NaCl solutions (>10 mmol/L); (2) CAS-bearing calcite is thermodynamically less stable than pure calcite and therefore exhibits higher solubility; and (3) NaCl leaching can remove other reduced sulfur-bearing phases, at least those present on exposed particle surfaces. Some studies have employed sodium hypochlorite (NaClO) and hydrogen peroxide (H₂O₂) leaching to remove pyrite and other reduced sulfur-bearing phases, thereby preventing sulfate derived from their oxidation from mixing with CAS during subsequent HCl dissolution of the carbonate. However, these oxidants often fail to completely eliminate pyrite and, more importantly, can generate new sulfate during the leaching process itself, introducing additional contamination [52,70–73]. Consequently, this non-CAS sulfate irreversibly contaminates the primary CAS extracted during the subsequent HCl dissolution step.

I demonstrated that a significant artifact in CAS stems from the contamination of outcropping carbonates in arid/semi-arid or polluted areas [74,75]. This contamination consists of secondary atmospheric sulfate (SAS), which forms from the atmospheric oxidation of sulfur gases such as SO₂ [76]. Using sequential leaching methods, $\delta^{18}\text{O}$, $\Delta^{17}\text{O}$, alongside $\delta^{34}\text{S}$, regardless of rock age, nearly all water-leachable sulfates and half of acid-leachable ones exhibit positive $\Delta^{17}\text{O}$ values (up to +1.4‰)—distinct from typical seawater sulfate (below zero). SAS is the only known source of such anomalies, arising from mass-independent fractionation involving O₃ [76,77]. This contamination lowers the $\delta^{34}\text{S}$ value of CAS (SAS averages ~1‰–4.5‰ vs. paleo-seawater 10‰–35‰), explaining the “super-heavy pyrite” enigma where $\delta^{34}\text{S}_{\text{CAS}}$ falls below co-occurring pyrite [78]. These findings necessitate a critical re-evaluation of existing outcrop-derived CAS data, many of which may be compromised by unrecognized SAS contamination. More crucially, systematic

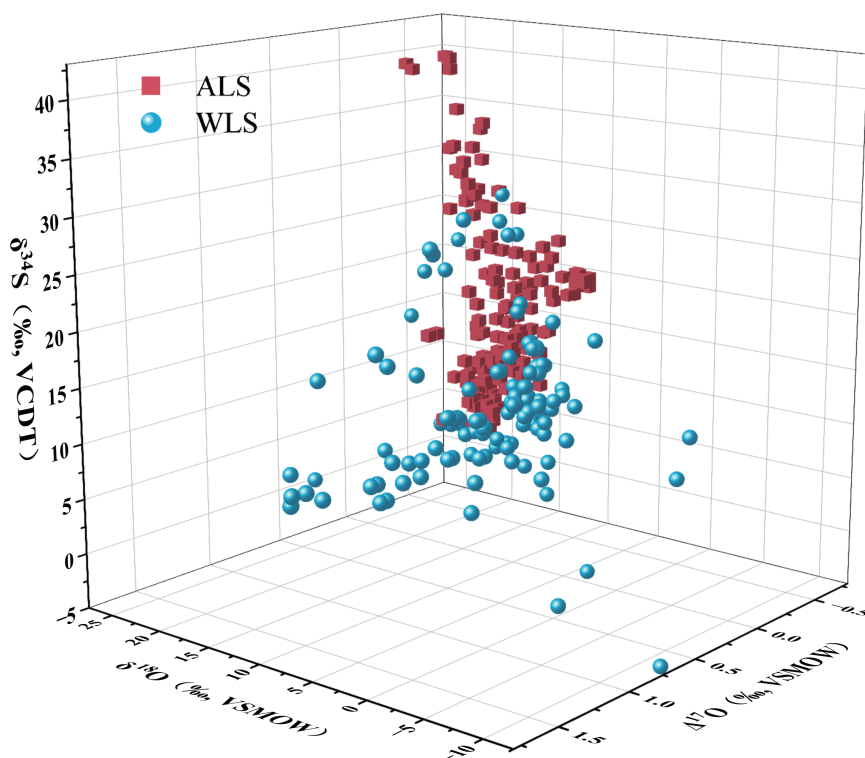


Figure 3 Spatial distribution of $\Delta^{17}\text{O}$, $\delta^{18}\text{O}$, and $\delta^{34}\text{S}$ signatures in different sulfate species. ALS: acid-leachable sulfate; WLS: water-leachable sulfate. SAS: secondary atmospheric sulfate; POS: pyrite oxidation sulfate, data from Refs. [32,74,75,79].

multi-isotope analysis ($\delta^{34}\text{S}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$) of sequentially extracted sulfate fractions, particularly the water-leachable and acid-leachable components, provides a robust diagnostic framework for identifying and excluding diagenetic overprints and exogenous contamination (Figure 3) [74].

By integrating insights from previous studies, I propose a standardized protocol for CAS extraction (Figure 4) [74]. Although this protocol is broadly applicable to most carbonate samples, several methodological uncertainties remain. Notably, the influence of grain size on CAS recovery has yet to be systematically evaluated. Moreover, despite the widespread adoption of 10% NaCl as a standard leaching condition [73,74,80], the optimal NaCl concentration for maximizing CAS extraction efficiency has not been rigorously constrained and warrants further investigation.

Barite purification

Although sulfur isotope analysis does not require additional purification following BaSO_4 precipitation, oxygen isotope analysis does, because a variety of oxygen-bearing phases including organic matter, clays, carbonates, nitrates, and phosphates, can co-precipitate with BaSO_4 and become physically associated with BaSO_4 . These contaminants can significantly bias $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values [81]. To ensure reliable oxygen isotope measurements, BaSO_4 must be further purified following precipitation. One established approach involves dissolution of BaSO_4 using diethylenetriaminepentaacetic acid (DTPA), followed by controlled reprecipitation, as originally described by Ref. [81]. Alternative purification strategies, Na_2CO_3 -based re-

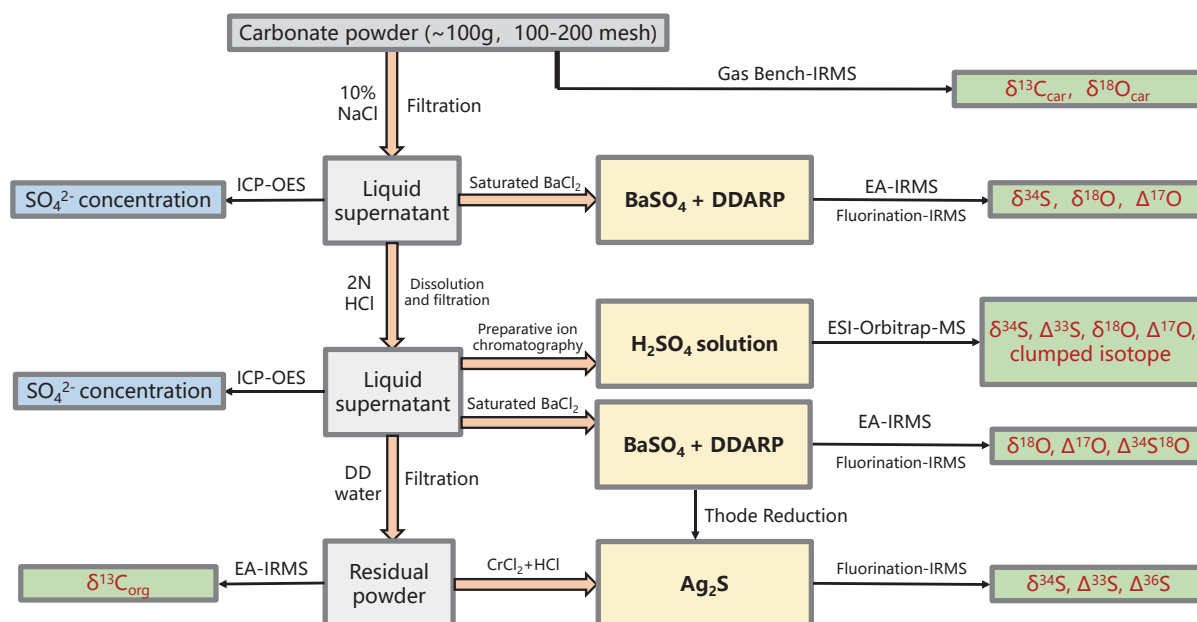


Figure 4 Recommended protocol for CAS extraction, purification, and isotope measurement.

precipitation methods, have also been employed in previous studies [82–84]. However, the relative efficiencies and potential biases associated with these different pretreatment approaches have not been systematically evaluated.

Isotope measurement

Conventional determinations of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ in barite rely on the quantitative conversion of sulfate to analyzable gaseous species for isotope ratio mass spectrometry (IRMS). For sulfur isotope analysis, IRMS coupled to an elemental analyzer (EA) is routinely employed. Purified BaSO_4 (typically 200–500 μg) is encapsulated in tin and combusted at $\sim 1000\text{--}1400\text{ }^\circ\text{C}$ in an oxygen-rich condition, commonly with the addition of vanadium pentoxide (V_2O_5) to promote complete oxidation. The resulting SO_2 is chromatographically separated, transported by a helium carrier gas, and analyzed by IRMS, yielding analytical precisions of approximately 0.1‰–0.5‰. Oxygen isotope analysis is performed using high-temperature conversion in a TC/EA or HT-EA system operated in Continuous flow mode. In this procedure, purified BaSO_4 (typically 200–300 μg) is sealed in silver capsules together with a glassy carbon reductant and pyrolyzed at temperatures exceeding $1400\text{ }^\circ\text{C}$, most commonly around $1450\text{ }^\circ\text{C}$. Under this reducing condition, sulfate oxygen is quantitatively converted to CO , which is subsequently separated by gas chromatography and introduced into the IRMS for isotopic analysis, achieving typical precisions of 0.3‰–0.5‰.

To simultaneously determine $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ and to calculate reliable $\Delta^{17}\text{O}$ values in barite, O_2 is generated as the analyte gas. Measurements are performed using IRMS in a dual-inlet mode, which allows high-precision analysis at masses O_2 as 32, 33, and 34. The most widely adopted approach involves CO_2 -laser fluorination to liberate oxygen directly from BaSO_4 , yielding analytical precisions of approximately 0.02‰ for $\Delta^{17}\text{O}$ [85]. In this method, 5–10 mg of barite powder is reacted with excess BrF_5 or F_2 in an evacuated

reaction chamber under CO₂-laser heating over 1000 °C, producing a partial but highly reproducible O₂ yield of approximately 25%–50%. The liberated O₂ is subsequently purified using a series of cold traps, sometimes supplemented by an in-line gas chromatograph, to remove fluorinated byproducts such as SOF₄, BrF₃, NF₃, and SF₆, etc. [86]. Because incomplete oxygen extraction—i.e., less than 100% yield—induces significant mass-dependent fractionation (typically an 8‰–14‰ offset in $\delta^{18}\text{O}$), $\delta^{18}\text{O}$ values are commonly determined independently using TC/EA.

A complementary approach developed by Ellis and Passey (2023) [87] employs high-temperature conversion-methanation-fluorination (HTC-M-F). In this method, barite mixed with accelerants such as graphite and AgCl or KF is pyrolyzed at temperatures exceeding 1400 °C in a glassy carbon reactor, quantitatively converting oxygen to CO. The CO is subsequently methanated to H₂O over an iron catalyst at 560 °C via the Bosch reaction, and the resulting H₂O is fluorinated to O₂ using solid CoF₃. Overall oxygen yields approach 89%–100%. The purified O₂ is analyzed by extended-integration dual-inlet IRMS, achieving a precision <0.01‰ (1 σ) for $\Delta^{17}\text{O}$.

Wei *et al.* (2024) [88] introduced the reduction-discharge-exchange (R-D-E) method, which achieves near-quantitative (~100%) recovery of sulfate oxygen. In this protocol, BaSO₄ powder is homogenized with graphite and reduced at 1000 °C in a platinum boat, producing CO and CO₂. Residual CO is converted to CO₂ via high-voltage electrical discharge (~3 kV) between platinum electrodes. The CO₂ is cryogenically trapped and subsequently isotopically equilibrated with reference O₂ over a hot platinum catalyst (750 °C for 1 h). The equilibrated O₂ is then analyzed by dual-inlet IRMS to determine $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ simultaneously. This method requires as little as 4 μmol of sulfate oxygen (~1 mg BaSO₄) and yields a $\Delta^{17}\text{O}$ precision better than 0.01‰ (1 σ).

Ellis *et al.* (2025) [89] describe a fluorination-free method coupling high-temperature conversion (HTC) to nickel-catalyzed CO-to-CO₂ conversion for laser spectroscopy. Barite oxygen is liberated as CO at 1450 °C in a glassy carbon reactor with excess glass carbon. CO is quantitatively converted to CO₂ over a heated nickel catalyst (350 °C) via the Boudouard reaction (2CO $\rightarrow$ C + CO₂). Conversion is rapid (10–30 min) and near 100% yield. The resulting CO₂ is analyzed by tunable infrared laser direct absorption spectroscopy (TILDAS), measuring multiple isotopologues simultaneously. Precision is about 0.01‰ (1 σ) for $\Delta^{17}\text{O}$ over months, with sample sizes of 1 mg BaSO₄.

For the determination of quadruple sulfur isotope compositions ($\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$), sulfate samples (typically ~2 mg BaSO₄) are initially converted to Ag₂S via Thode reduction procedure [90,91]. The resulting Ag₂S is subsequently fluorinated using BrF₅ or F₂ to generate SF₆. Fluorination byproducts are removed through a series of cold traps, commonly augmented by an in-line gas chromatographic purification step. The purified SF₆ is then analyzed for $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$ using IRMS (e.g., Thermo MAT253) with dual-inlet mode, achieving external precisions of 0.02‰, 0.003‰, and 0.1‰ (1 σ) for $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$, respectively [92]. Measuring $\delta^{36}\text{S}$ is challenging due to the low abundance of ³⁶S and isobaric interference at m/z 131, primarily from C₃F₅⁺ derived from fluorinated hydrocarbon fragmentation. The advent of ultra-high-resolution IRMS (e.g., MAT 253 Ultra) now enables baseline separation of ¹²C₃F₅⁺ from ³⁶SF₅⁺. This advance has improved the external precision of $\Delta^{36}\text{S}$ analysis to 0.07‰ [93]. To accommodate sub-micromole sulfur samples, Ueno *et al.* (2015) [94] developed a rapid “flash-fluorination” technique employing cobalt trifluoride (CoF₃). In this approach, Ag₂S is mixed with CoF₃ and flash-heated to ~590 °C for ~3 s using a Curie-point pyrolyzer, producing SF₆ that is purified cryogenically prior to IRMS analysis. Long-term

analytical reproducibility is typically 0.4‰ for $\delta^{34}\text{S}$, 0.01‰ for $\Delta^{33}\text{S}$, and 0.1‰ for $\Delta^{36}\text{S}$. This method can be readily extended to sulfide minerals (e.g., pyrite) and organic sulfur compounds, and offers improved safety and operational simplicity relative to conventional F_2 or BrF_5 fluorination.

An alternative approach employs multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) for the determination of $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values of sulfate. Long-term reproducibility is typically 0.2‰ for $\delta^{34}\text{S}$ and 0.05‰ for $\Delta^{33}\text{S}$ (2σ) [95]. Analyses are conducted in high-resolution mode ($M/\Delta M \approx 8000$ – $10,000$) to resolve isobaric interferences from O_2 and SH species on ^{32}S , ^{33}S , and ^{34}S ions. Samples are introduced as dissolved Na_2SO_4 in 5% HNO_3 solution and enabling measurements on as little as 5–30 nmol of sulfur. Despite these advantages, analytical precision remains inferior to that achieved by SF_6 -IRMS (e.g., $\Delta^{33}\text{S}$ precision of about 0.02‰ compared to $\sim 0.005\text{‰}$ – 0.01‰ for SF_6 -IRMS), limiting the resolution of subtle mass-dependent fractionation (MDF) signals. In addition, ^{36}S cannot be measured due to interference from ^{36}Ar derived from the plasma gas. Nevertheless, MC-ICP-MS offers substantial benefits for geochemists working with trace sulfate in limited or dilute matrices, such as ice cores or CAS of Precambrian carbonates, where only nanomole-level sulfur is available. Sample preparation is relatively straightforward, requiring no gas conversion; instead, samples undergo dissolution, oxidation (for sulfides), and ion-exchange purification. This simplicity significantly improves analytical throughput and accessibility relative to SO_2 - or SF_6 -based methods.

A new approach designed to analyze clumped isotopes of sulfate in BaSO_4 by means of low-temperature fluorination and High-Resolution gas source isotope ratio mass spectrometry (HR-IRMS, e.g., Thermo MAT253 Ultra) in products of SO_2F_2 (e.g., $^{36}\text{S}^{16}\text{O}_2\text{F}_2$, $^{34}\text{S}^{18}\text{O}^{16}\text{OF}_2$, and $^{32}\text{S}^{18}\text{O}_2\text{F}_2$) has been established. The reproducibility of the $\Delta^{34}\text{S}^{18}\text{O}$ value in the entire process from fluorination is 0.17‰ [24,96]. This approach also shows high precision in measuring $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\delta^{18}\text{O}$ (Table 1).

Moreover, recent advancements have enabled the coupling of Orbitrap MS with electrospray ionization (ESI), facilitating the precise analysis of naturally abundant stable isotopes in oxyanions [97,98]. This method enables the direct analysis of multiple isotopologues of SO_4^{2-} with the significant advantage of reduced sample consumption. This capability opens new avenues for revisiting longstanding questions in biogeochemical cycles across both modern and geological time scales. For measurements of $\delta^{18}\text{O}$, $\delta^{17}\text{O}$, $\delta^{34}\text{S}$, $\delta^{33}\text{S}$, and $\delta^{36}\text{S}$ —as well as clumped isotopes (e.g., $\Delta^{34}\text{S}^{18}\text{O}$), ESI-Orbitrap-MS only acquires a single sulfate aliquot injection with sample size at the nano-mole level, eliminating the need for chemical conversion of sulfate into an analyte like SF_6 or O_2 . While current analytical precision is lower than that achieved by IRMS, ESI-Orbitrap-MS offers a valuable and largely untapped opportunity to investigate clumped isotopes of sulfate.

APPLICATIONS IN TRIPLE OXYGEN ISOTOPES OF CAS

Bao (2015) [23] provides a comprehensive review of triple oxygen isotope systematics in sulfate. In summary, mass-independent fractionation (MIF; $\Delta^{17}\text{O} \neq 0$) in the Earth system arises predominantly from atmospheric photochemical processes, especially ozone (O_3) formation and destruction in the ozone-rich stratosphere [99,100]. Within the Chapman reaction framework of the O_3 - CO_2 - O_2 system, oxygen-atom

Table 1 Summary of analytical techniques for sulfur-oxygen isotope measurement of barite/sulfate

Technique	Analysis amount/sample	Analysis cost time/sample (min)	Analysis precision (‰)					
			$\Delta^{17}\text{O}$	$\delta^{18}\text{O}$	$\Delta^{33}\text{S}$	$\delta^{34}\text{S}$	$\Delta^{36}\text{S}$	$\Delta^{34}\text{S}^{18}\text{O}$
EA-IRMS [94]	~1 μmol	~10	—	0.3	0.5	0.3	—	—
Laser fluorination + IRMS [85]	~25 μmol	~60	0.05	0.8	—	—	—	—
HTC-M-F [87]	~7 μmol	~100	0.004	0.3	—	—	—	—
R-D-E [88]	~4 μmol	~100	0.009	0.14	—	—	—	—
HTC + NiCO ₃ + TILDAS [89]	~7 μmol	~75	0.01	0.2	—	—	—	—
SF ₆ + IRMS [92,93]	~8 μmol	~100	—	—	0.003	0.02	0.07	—
MC-ICP-MS [95]	~15 nmol	~3	—	—	0.1	0.2	—	—
Low-T SO ₂ F ₂ + HR-IRMS [24,96]	~25 μmol	>180	—	0.04	0.02	0.01	—	0.17
ESI-Orbitrap MS [97,98]	~25 nmol	~100	~0.5	~0.5	~0.2	~0.2	~1	~1

exchange mediated by excited $\text{O}(^1D)$ generates molecular oxygen characterized by negative $\Delta^{17}\text{O}$ values and ozone enriched in positive $\Delta^{17}\text{O}$ [100–102]. The resulting $\Delta^{17}\text{O}$ of tropospheric O_2 is further influenced by atmospheric p_{CO_2} and p_{O_2} , as well as by biosphere O_2 fluxes associated with primary productivity, respiration, and oxidative weathering [22,103,104]. These mass-independent signatures are transferred to secondary oxidation products such as sulfate, with negative $\Delta^{17}\text{O}$ contributions inherited from O_2 and positive contributions from O_3 [23,36]. At present, atmospheric photochemistry is the only well-established mechanism capable of producing oxygen-isotope MIF [105,106]. Consequently, $\Delta^{17}\text{O}$ in sulfate serves as a uniquely diagnostic tracer of sulfate sources, formation pathways, and oxidative cycling in surface environments [107]. More broadly, sulfate oxygen isotopes retain direct imprints of atmospheric O_2 and O_3 , making sulfate arguably the most robust—and potentially the only—geochemical archive of past O_2 and O_3 in Earth's surface system (Figure 5) [23].

Marine sulfate is primarily sourced from continental pyrite oxidative weathering and evaporite gypsum dissolution [7]. Laboratory experiments confirm 20%–30% atmospheric O_2 incorporation into sulfate during pyrite or sulfite oxidation [108–110]. Modern river sulfate $\Delta^{17}\text{O}$ values for the Mississippi and Yellow Rivers range from -0.19‰ to -0.01‰ , based on samples analyzed at the Bao lab in Louisiana State University [111,112]. In contrast, Hemingway *et al.* (2020) [113] reported positive $\Delta^{17}\text{O}$ values ranging from 0.041‰ to 0.18‰ for sulfate in the Marsyangdi River, with samples analyzed at the Johnston lab in Harvard University. This discrepancy arises from differences in measurement methods, as confirmed by Wei *et al.* (2024) [88]. Both labs employed CO_2 -laser heating to fluorinate solid BaSO_4 into O_2 gas, but this approach results in incomplete recovery of SO_4^{2-} oxygen, introducing uncertainty. Specifically, the Bao lab used BrF_5 as the oxidant, while the Johnston lab used F_2 . Wei *et al.* (2024) [88] determined that sulfate $\Delta^{17}\text{O}$ values measured from partially yielded O_2 in fluorination techniques are 0.01‰ – 0.20‰ higher than those obtained via the R-D-E method, depending on the oxidant (e.g., F_2 or BrF_5). For the international sulfate reference material NBS-127, $\Delta^{17}\text{O}$ measured by F_2 laser fluorination is $\sim 0.09\text{‰}$ higher than with BrF_5 . Critically, application of the R-D-E method demonstrated that incomplete sulfate reduction leads to systematically lower $\delta^{18}\text{O}$ values and elevated $\Delta^{17}\text{O}$ values, and it enabled recalibration of the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values of international reference materials NBS-127, IAEA-SO-5, and IAEA-SO-6 on the VSMOW-SLAP scale.

According to the modern $\Delta^{17}\text{O}$ interpretation framework, marine sulfates with negative $\Delta^{17}\text{O}$ values or those derived from oxidative weathering are expected to emerge after the Great Oxidation Event (GOE) at

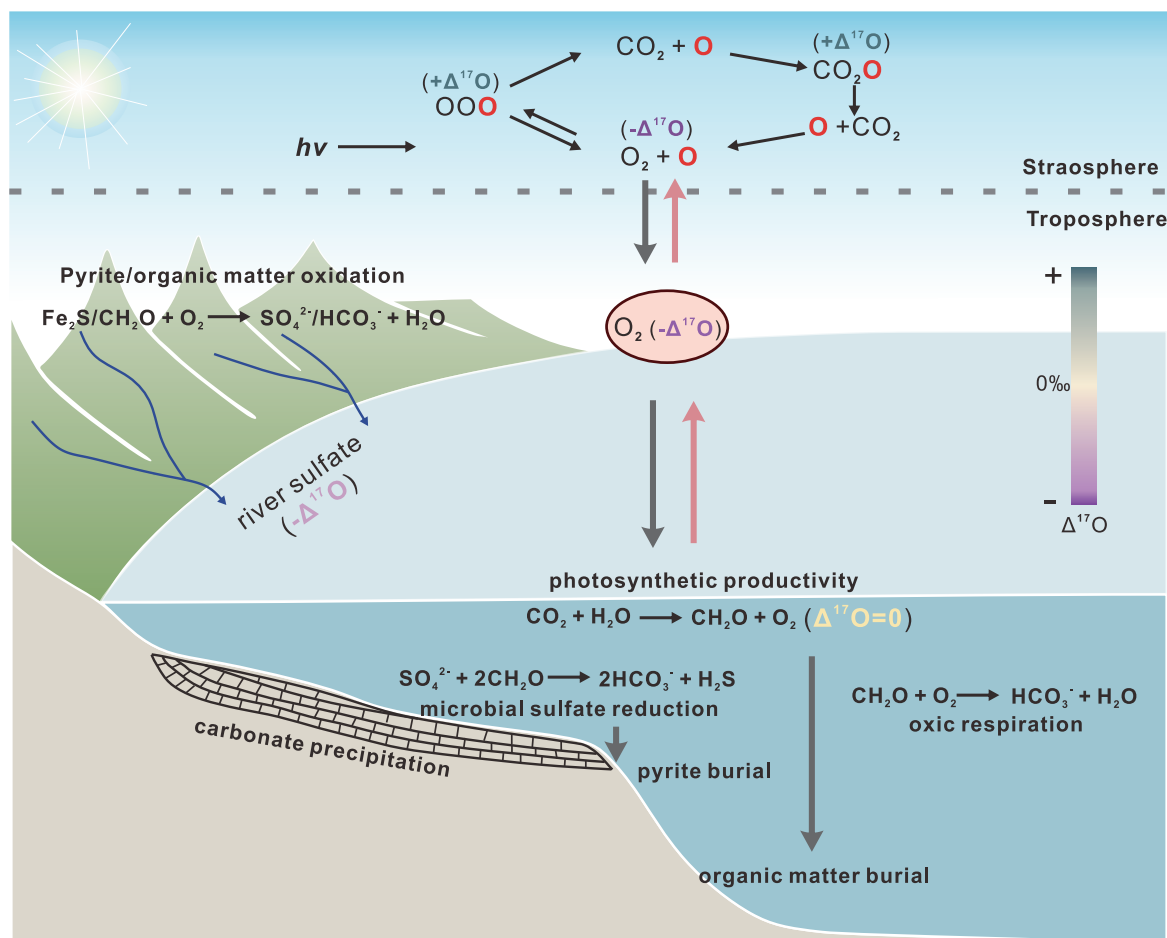


Figure 5 A schematic illustration of oxygen fluxes among the atmosphere, biosphere, and ocean in the Earth's surface system. The upper panel depicts the photochemical reaction network involving O_2 , O_3 , and CO_2 in the atmosphere, highlighting mass-independent oxygen isotope fractionation. Red O denotes the heavy oxygen isotopes (^{17}O and ^{18}O), illustrating how O_2 becomes depleted in these isotopes as a result of stratospheric photochemical processes before being transported to the lower atmosphere. The lower panel illustrates the coupled surface cycling of carbon, oxygen, and sulfur. Atmospheric O_2 oxidizes sulfide minerals (e.g., pyrite), producing sulfate characterized by negative $\Delta^{17}O$ signatures, which is subsequently delivered to the ocean via riverine transport. In the marine system, sulfate reduction and pyrite burial act as major sinks for sulfur, linking the sulfur cycle to the long-term regulation of atmospheric oxygen levels.

about 2.3 Ga, when atmospheric O_2 levels exceeded $\sim 10^{-5}$ of present atmospheric levels (PAL), and O_3 began forming [114]. However, it was not until Bao *et al.* (2008) [36] first reported highly negative $\Delta^{17}O$ values (down to -0.7‰) in barite crystal fans overlying cap carbonates of the Marinoan (~ 635 Ma) glacial diamictites. Subsequent studies confirmed the global extent of this Marinoan Oxygen-17 Depletion (MOSD) event [37,104,115–117]. Bao *et al.* (2009) [118] later identified even more extreme negative $\Delta^{17}O$ values (as low as -1.64‰) in CAS extracted from carbonate lenses within Marinoan glacial diamictites from Svalbard, where elevated CAS concentrations indicate localized evaporative settings rather than open-marine conditions. Cao and Bao (2013) [119] developed a coupled four-box biosphere-atmosphere model to simulate both steady-state and dynamic aspects of the MOSD. Their modeling not only demonstrated that ultra-high p_{CO_2} levels invoked by the Snowball Earth hypothesis could generate a typical MOSD duration of $<10^6$ years with $\Delta^{17}O$ magnitudes of atmosphere oxygen approaching -35‰ , but also established a theoretical framework for

leveraging $\Delta^{17}\text{O}$ to reconstruct ancient atmospheric p_{CO_2} , p_{O_2} , and biospheric productivity.

Crockford *et al.* (2018) [104] report the most negative $\Delta^{17}\text{O}$ values (-0.88‰) outside the Cryogenian, with no S-MIF, indicating oxygenated conditions ($p_{\text{O}_2} > 0.1\%$ PAL) from ~ 1.4 Ga gypsum nodules from the lacustrine-sabkha Sibley Group, Ontario, Canada. Hodgskiss *et al.* (2019) [120] examined ~ 20 Ga barites from the Belcher Group, Nunavut, Canada, capturing immediate post-GOE conditions. Negative $\Delta^{17}\text{O}$ ($\sim -0.8\text{‰}$), $\delta^{34}\text{S}$ ($\sim +21\text{‰}$), negative $\Delta^{33}\text{S}$, and marine-like $\delta^{138}\text{Ba}$ indicate remobilized sulfate from older evaporites mixed with seawater Ba, preserving syn-GOE atmospheric anomalies. These two studies interpreted that the large negative sulfate $\Delta^{17}\text{O}$ signatures were generated under conditions of relatively low primary productivity when atmospheric CO_2 and O_2 concentrations are at the same magnitude, as predicted by a modeling study [119]. These early investigations provided qualitative insights into p_{CO_2} and p_{O_2} but lacked precise quantification, relying primarily on barite and evaporite archives that offered limited temporal resolution and single-proxy perspectives. This constrained their ability to integrate multiple indicators for testing coupled C-O-S cycles and constraining inter-element relationships. Such studies underscore the need for integrated geochemical modeling to quantify ancient atmosphere-biosphere dynamics.

Therefore, CAS emerges as an ideal proxy for a multi-proxy approach that provides temporal evolution across geologic time, linking C-O-S cycles. Bao *et al.* (2012) [121] examine CAS in Neoproterozoic cap dolostones from the Kimberley region, Western Australia, focusing on the Marinoan glaciation (~ 635 Ma). They report pronounced negative $\Delta^{17}\text{O}$ values (down to -0.68‰) in CAS from the Moonlight Valley (MV) cap dolostones at the Texas/Mabel Downs (TMD) section, proximal to paleo-continent, where oxidative weathering of sulfides likely transferred atmospheric O_2 's non-mass-dependent depletion. In contrast, the Palm Spring (PS) section, in an open-ocean setting ~ 150 km away, and the younger Egan cap dolostones show no such anomalies ($\Delta^{17}\text{O}$ near 0‰). Accompanied by $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ data of CAS, these findings link the signal's presence to continental runoff and its absence to marine dilution or microbial overprinting. In biologically active water columns or the water-sediment interface in oceans or lakes, microbial sulfate reduction (MSR) eliminates $\Delta^{17}\text{O}$ signals as sulfate exchanges oxygen with ambient water via reversible enzyme steps [31,122]. Meanwhile, sulfide is re-oxidized to sulfate by dissolved O_2 with a $\Delta^{17}\text{O}$ value that is less negative than that of atmospheric O_2 , depending on rates of photosynthesis, respiration, and air-water gas exchange. So, the sulfide re-oxidation process can also diminish the ^{17}O MIF signature during microbially active S cycling in modern aerobic aquatic environments. Crockford *et al.* (2025) [123] extend this to mid-Proterozoic (~ 2.0 – 1.0 Ga) sulfates, analyzing evaporites, barites, and CAS. They identify a clear environmental gradient: terrestrial/lacustrine settings preserve the most negative and variable $\Delta^{17}\text{O}$ (down to -1.7‰), consistent with direct pyrite oxidation incorporating atmospheric O_2 's MIF signal, while marine environments yield values near modern seawater sulfate ($\sim 0\text{‰}$), indicating dilution by seawater sulfate reservoirs or biogeochemical recycling.

Together, these papers confirm that $\Delta^{17}\text{O}$ in CAS is not a uniform global proxy but depends on depositional conditions—strongest near continents/terrestrial sources due to undiluted oxidative weathering, and muted in open-marine settings by mixing and cycling. This has implications for reconstructing p_{O_2} , p_{CO_2} , and productivity: interpretations must account for paleogeography and sedimentology to avoid conflating local artifacts. Building on the recognition that CAS can incorporate ambient aqueous sulfate and experience diagenetic overprinting that may obscure primary atmospheric $\Delta^{17}\text{O}$ signals, the extraction of robust paleo-

atmospheric records remains challenging. Early studies focused primarily on absolute $\Delta^{17}\text{O}$ values in CAS but paid limited attention to stratigraphic or temporal variability and to integration with complementary proxies such as $\delta^{13}\text{C}$, $\delta^{34}\text{S}$, and $\delta^{18}\text{O}$, which are essential for resolving coupled carbon, oxygen, and sulfur cycle dynamics. These complexities set the stage for the pivotal work of Wang *et al.* (2023) [32], which tackles the long-standing enigmatic Ediacaran Shuram Excursion (SE)—the largest negative $\delta^{13}\text{C}$ excursion in Earth history ($\sim 574\text{--}567\text{ Ma}$) [124], lasting approximately 7 Myr [125]. The SE is globally expressed in carbonate successions, where $\delta^{13}\text{C}$ values decline from about $+5\text{‰}$ to -12‰ and has been widely debated as either a primary signal of global ocean oxidation or a product of diagenetic overprinting [126,127]. Wang *et al.* (2023) [32] investigate this problem by CAS from three geographically and tectonically distinct paleocontinents: the Doushantuo Formation (South China), the Wonoka Formation (South Australia), and the Shuiquan Formation (Tarim). CAS was extracted using rigorous NaCl-HCl leaching protocols designed to eliminate contaminants such as modern atmospheric sulfate and pyrite-derived artifacts. The data reveal exceptionally negative $\Delta^{17}\text{O}$ values in CAS, reaching -0.53‰ in South China, -0.51‰ in South Australia, and -0.35‰ in Tarim—values far more negative than typical Phanerozoic sulfate ($\sim -0.07\text{‰}$). Stratigraphic trends closely track $\delta^{13}\text{C}$ behavior, with an initial decrease in $\Delta^{17}\text{O}$ followed by recovery and exhibit coherent covariation with $\delta^{34}\text{S}$ ($10.2\text{‰--}42.0\text{‰}$) and $\delta^{18}\text{O}$ ($8.0\text{‰--}23.1\text{‰}$). In contrast, NaCl-leached fractions yield less negative $\Delta^{17}\text{O}$ and lower $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values, consistent with contamination, whereas HCl-leached fractions preserve primary isotopic signatures. Cross-plots converge toward low $\delta^{18}\text{O}$ ($\sim 12\text{‰}$) and $\delta^{34}\text{S}$ ($\sim 18\text{‰}$) at the SE nadir, implying a globally uniform sulfate source during this interval. They attribute these anomalies to MIF in atmospheric O_2 , subsequently transferred to sulfate during sulfide oxidation. The pronounced negative $\Delta^{17}\text{O}$ values effectively exclude diagenetic alteration, as no known diagenetic process can generate such signals; meteoric infiltration or burial alteration would tend to homogenize isotopic compositions rather than produce coherent, globally consistent trends. Evaporite dissolution is likewise rejected, as pre-Ediacaran evaporites lack significant ^{17}O depletions, are volumetrically insufficient, and cannot account for the observed uniform multi-isotope patterns across continents. A non-steady-state sulfur-cycle box model further constrains the underlying processes. The modeling demonstrates that enhanced continental pyrite weathering alone cannot reproduce the observed isotopic shifts without invoking implausible increases in weathering fluxes ($>100\text{-fold}$) and unrealistically high seawater sulfate concentrations ($\sim 300\text{ mmol/L}$). Instead, the best fit is achieved through large-scale water-column ventilation, characterized by diminished microbial sulfate reduction, enhanced aerobic re-oxidation of H_2S , and episodic oxidation of pre-existing marine H_2S and S^0 reservoirs. Ventilation of sulfidic deep waters introduces ^{17}O -depleted atmospheric O_2 into the ocean, while suppressed sulfate reduction buffers oxygen isotope signals. This mechanism also provides a coherent explanation for the characteristic $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ and $\delta^{34}\text{S}$ - $\Delta^{17}\text{O}$ relationships observed in basal Ediacaran barite [117].

These findings have far-reaching implications for Neoproterozoic redox evolution. The Shuram Excursion is best interpreted as recording sustained oxidation of ^{13}C -depleted organic carbon reservoirs such as dissolved organic carbon and hydrocarbons, driven by the incursion of atmospheric O_2 into the ocean, rather than by localized photosynthetic production or evaporite recycling. Occurring approximately 60 Myr after the Marinoan glaciation-related ^{17}O depletions, the SE implies episodic oxygenation of the Earth system and suggests low, spatially heterogeneous pre-SE seawater sulfate concentrations on the order of $\sim 1\text{ mmol/L}$. The coupled behavior of carbon, sulfur, and oxygen isotopes robustly links sulfur cycling to global carbon-cycle perturbations, supporting a primary, globally coherent origin for the SE and directly challenging diagenetic

interpretations. Equally significant, these data represent the first documentation of post-Snowball Earth negative ^{17}O anomalies preserved in CAS, underscoring the importance of stratigraphic trends and relative variations rather than absolute isotope values.

Based on those early investigations, Wang *et al.* (2025) [128] compile a comprehensive $\Delta^{17}\text{O}$ dataset ($n = 1,806$), with 287 new CAS measurements from carbonates spanning $\sim 1.0\text{--}0.4$ Ga, supplemented by barite ($n = 16$) and gypsum ($n = 17$). The results show that sulfate $\Delta^{17}\text{O}$ values exhibit distinct three-stage changes on billion-year timescales, corresponding to three key oxygen content increases in the Paleoproterozoic, Neoproterozoic, and Paleozoic eras, ultimately stabilizing around 410 Ma, marking the formal establishment of the modern oxygen-rich atmospheric environment. More importantly, following the Neoproterozoic atmospheric oxygen content leap, the predominantly anoxic marine system experienced periodic oxidative enhancements, manifested as recurrent significant negative excursions in carbonate $\delta^{13}\text{C}$, accompanied by consistent declines in sulfate $\Delta^{17}\text{O}$ and $\delta^{34}\text{S}$. Combining quantitative analysis from the NEOCARBSULF biogeochemical model and the $\text{O}_2\text{--CO}_2$ box model, they interpret these coupled C-S-O isotope perturbations as reflecting pulsed oxidation of the anoxic ocean by episodically elevated atmospheric oxygen. This process promoted the oxidation of dissolved organic carbon and reduced sulfur in the ocean, producing large amounts of sulfate and inorganic carbon with depleted $\Delta^{17}\text{O}\text{--}\delta^{34}\text{S}\text{--}\delta^{13}\text{C}$ characteristics, leading to the synchronized changes in these three isotopes on million-year timescales. At the same time, this process acted as a negative feedback mechanism that rapidly consumed atmospheric oxygen in the short term, thereby inhibiting and reversing the sustained rise in atmospheric oxygen content. These findings indicate that the oxidation states of the atmosphere and ocean exhibit positive feedback co-evolution on billion-year timescales, while on million-year timescales, they may display negative feedback regulation. In other words, million-year-scale negative feedback regulation is superimposed on the overall trend of atmospheric-oceanic oxidation enhancement on billion-year timescales, revealing the highly nonlinear and multi-scale feedback regulation mechanisms in Earth's surface system oxidation processes. This constructs a gradual dynamic oxidation framework for Earth's surface spanning two billion years. The study further reveals the co-evolutionary mechanisms between the atmosphere and ocean during this long, gradual dynamic oxidation process, providing a theoretical foundation for understanding the anomalous carbon isotope records from the Neoproterozoic to early Paleozoic and the prolonged yet episodically rapid evolution of complex eukaryotic life. Future applications could refine GPP estimates and explore spatial heterogeneities, advancing our understanding of habitability transitions.

The $\Delta^{17}\text{O}$ value of WLS is commonly used as an indicator to assess whether CAS has been affected by post-depositional contamination. Analyzing over 20 years of lab isotope data, we unexpectedly addressed pre-industrial aerosol uncertainties in climate models. These natural emissions (biological, fire, volcanic) form background forcing; uncertainties amplify future projections. A key assumption of Andreae [129] posits that pre-anthropogenic continental cloud microphysics mirrored oceanic ones. Leveraging the 2014 protocol, Peng *et al.* (2023) [75] identified a pre-industrial sulfate aerosol (SAS) endmember preserved in carbonates from northern China and the southwestern U.S., characterized by $\Delta^{17}\text{O}$ values of approximately $+1.8\text{‰}$, $\delta^{18}\text{O}$ ranging from -1‰ to 5‰ , and $\delta^{34}\text{S}$ between -5‰ and 10‰ . These values contrast sharply with those of modern anthropogenic SAS, which exhibit $\Delta^{17}\text{O}$ of $0.5\text{‰}\text{--}0.6\text{‰}$, $\delta^{18}\text{O}$ of $11\text{‰}\text{--}15\text{‰}$, and $\delta^{34}\text{S}$ of $1\text{‰}\text{--}4.5\text{‰}$. GEOS-Chem modeling confirmed higher past $\Delta^{17}\text{O}$ in these regions, akin to modern Southern Hemisphere pristine oceans, supporting Andreae's hypothesis. Pre-industrial SAS implied higher cloud-water pH, cleaner

air, and coarser aerosols, potentially yielding less cloud cover than today. Future work, collecting global outcrop sulfate isotopes, can refine isotope-constrained transport models, infer SAS formation pathways affecting aerosol microphysics, and constrain pre-industrial particle sizes, cloud nuclei, and radiative forcing—reducing climate prediction uncertainties. This isotope approach powerfully disentangles anthropogenic from natural sulfur baselines.

APPLICATIONS IN QUADRUPLE SULFUR ISOTOPES OF CAS

Current studies on quadruple sulfur isotopes in CAS can be broadly divided into two categories. The first targets the period before the Great Oxidation Event (GOE), focusing on the origin of sulfur mass-independent fractionation (S-MIF) in the Archean atmosphere [130–132]. The second investigates sulfur mass-dependent fractionation (S-MDF) after the GOE, particularly the evolution of marine sulfur cycling throughout the Proterozoic and Phanerozoic [20,133–137]. Nevertheless, published studies remain limited. This is mainly because sulfate concentrations in Archean seawater were extremely low, resulting in very low CAS contents in carbonate rocks and making it challenging to extract enough material for multiple-sulfur isotope analyses. In addition, after the GOE, $\Delta^{33}\text{S}$ variations in dissolved seawater sulfate are extremely small, making it difficult to infer internal marine sulfur cycle dynamics solely from the $\Delta^{33}\text{S}$ of sulfate.

Before the end of the Archean (~2.4 Ga), S-MIF signals were widespread in the geological record and provided critical constraints on the timing of the GOE [28,138,139]. When atmospheric oxygen levels were below $\sim 10^{-5}$ PAL, an ozone layer could not form [140,141]. Consequently, UV penetrated the troposphere and drove photochemical reactions that produced strong S-MIF signals in sulfur-bearing species [28]. According to the classical Archean sulfur cycle model proposed by Farquhar *et al.* (2001) [142], volcanic SO_2 was photolyzed in the atmosphere, yielding elemental sulfur with positive $\Delta^{33}\text{S}$ anomalies and sulfate with negative $\Delta^{33}\text{S}$ anomalies. This model has been validated by laboratory photochemical chamber experiments and by multiple-sulfur isotope signatures preserved in early Archean barite.

However, CAS extracted from late Archean (2.7–2.5 Ga) carbonates exhibits large positive $\Delta^{33}\text{S}$ anomalies similar to those in coeval pyrite, which contradicts the predictions of the classical photochemical model. These observations imply that atmospheric sulfur cycling mechanisms may have changed during the late Archean, potentially due to rising oxygen levels that modified photochemical pathways and produced sulfate with positive $\Delta^{33}\text{S}$ [143,144]. Nevertheless, the origin of these CAS signals remains uncertain. It is unclear whether the measured CAS reflects primary seawater sulfate signatures or is affected by later alteration processes, such as contamination from pyrite during extraction. Future studies could employ ESI-Orbitrap-MS to measure oxygen isotopes in CAS, enabling direct assessment and discrimination of diagenetic or primary signal.

Post-GOE research on CAS multiple-sulfur isotopes focuses on S-MDF. Such studies often combine CAS and pyrite $\Delta^{33}\text{S}$ data to diagnose microbial sulfur metabolisms within the $\Delta^{33}\text{S}$ - $\delta^{34}\text{S}$ framework. Different microbial processes impose distinct kinetic effects and thus create varying degrees of isotopic exchange among sulfur species, leading to characteristic $^{33}\theta$ values that follow different S-MDF laws [26,145–148]. For example, compared with dissimilatory sulfate reducers, sulfur-disproportionation and sulfide-oxidizing microbes preferentially incorporate ^{33}S during metabolism, producing $^{33}\theta$ values greater than 0.515 [149].

Therefore, paired analyses of CAS (representing seawater sulfate) and pyrite have been widely applied to constrain the emergence and evolution of oxidative sulfur cycling in Earth's history and to reconstruct the S-MDF characteristics of ancient seawater sulfate [133,147].

APPLICATIONS IN $\Delta^{34}\text{S}$ VERSUS $\Delta^{18}\text{O}$ OF CAS

The coupled behavior of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ in sulfate constitutes a powerful proxy for interrogating MSR, particularly when linked to anaerobic oxidation of methane (AOM). This dual-isotope ($\delta^{34}\text{S}$ vs. $\delta^{18}\text{O}$) framework capitalizes on the contrasting fractionation systematics of sulfur and oxygen during MSR, thereby providing quantitative constraints on redox dynamics in modern marine sediments as well as in ancient depositional environments. During bacterial sulfate reduction (BSR), sulfate is reduced to sulfide through a sequence of largely reversible, enzyme-mediated steps, including activation to adenosine 5'-phosphosulfate (APS), reduction to sulfite, and subsequent reduction to sulfide. Antler *et al.* (2013) [65] demonstrated that the slope of $\delta^{18}\text{O}$ vs. $\delta^{34}\text{S}$ in pore-water sulfate is systematically related to the net sulfate reduction rate (nSRR). High nSRR settings, such as estuarine sediments, are characterized by shallow slopes ($\sim 0.1\text{--}0.3$), reflecting limited sulfite reoxidation and recycling: sulfur isotopes evolve rapidly, whereas oxygen isotopes change more slowly due to incomplete equilibration with ambient water. In contrast, low nSRR environments, such as deep-sea sediments, exhibit steeper slopes (>0.5), consistent with extensive intracellular recycling ($>99\%$) that promotes enhanced oxygen isotope exchange between sulfate intermediates and water. Building on this framework, Antler *et al.* (2015) [150] identified diagnostic $\delta^{18}\text{O}\text{--}\delta^{34}\text{S}$ signatures associated with sulfate-driven AOM at methane seeps. In bubbling cold seeps, where methane supply exceeds sulfate availability, $\delta^{18}\text{O}\text{--}\delta^{34}\text{S}$ slopes are relatively low ($\sim 0.24\text{--}0.4$), distinct from those produced by organotrophic MSR or diffusion-limited AOM (>0.4). These low slopes reflect rapid sulfate reduction with minimal reoxidation and recycling. Importantly, this isotopic approach can be extended to the geological record through analyses of CAS, providing a means to identify paleo-methane seep environments and to reconstruct past MSR-AOM dynamics.

To test this framework, Feng *et al.* (2016) [151] analyzed CAS from three modern methane-seep provinces—the Gulf of Mexico, the Black Sea, and the South China Sea—and from two ancient seep systems, including Neogene deposits in northern Italy and Paleogene strata in western Washington (USA). The dataset encompasses both aragonite- and calcite-dominated carbonates and integrates measurements of $\delta^{18}\text{O}_{\text{CAS}}$, $\delta^{34}\text{S}_{\text{CAS}}$, CAS concentrations, pyrite $\delta^{34}\text{S}$, carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, as well as $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Across all sites and ages, the results reveal consistently low $\delta^{18}\text{O}_{\text{CAS}}/\delta^{34}\text{S}_{\text{CAS}}$ slopes ($\sim 0.28\text{--}0.32$), closely matching the shallow slopes ($0.24\text{--}0.4$) observed in modern methane-rich pore fluids influenced by sulfate-driven AOM. These values are distinctly lower than the steeper slopes (>0.4) characteristic of organotrophic sulfate reduction or diffusion-limited methane systems. Mineral-specific differences further refine this interpretation. Aragonite samples display steeper slopes (~ 0.53), higher CAS contents (~ 249 ppm), and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios close to modern seawater (0.709175), consistent with precipitation in shallow, seawater-influenced pore fluids with relatively high sulfate availability. In contrast, calcite samples exhibit gentler slopes (~ 0.30), lower CAS concentrations (~ 188 ppm), and more variable $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.708357–0.710124), indicative of deeper pore-fluid environments where sulfate is more depleted and isotopically evolved as a result of

intense sulfate-driven AOM. Together, these patterns demonstrate that CAS faithfully records the isotopic fingerprint of sulfate-driven AOM—characterized by preferential removal of ^{32}S into sulfides and extensive oxygen isotope exchange between sulfate intermediates and water without significant diagenetic overprinting. The robustness of this proxy is further supported by the observation that $\delta^{18}\text{O}/\delta^{34}\text{S}$ slopes are largely insensitive to environmental parameters such as temperature or salinity and are consistent with mechanistic models invoking sulfur-intermediate re-oxidation in methane-fueled systems. Importantly, this study also confirms that CAS incorporated carbonates are derived predominantly from pore fluids rather than directly from overlying seawater.

The strongly ^{13}C -depleted calcite cements ($\delta^{13}\text{C} < -30\text{‰}$) occurring in Ediacaran cap carbonates deposited immediately after the Marinoan Snowball Earth (~ 635 Ma) were originally interpreted as products of coupled sulfate-driven AOM [152]. This interpretation implied unusually high marine sulfate concentrations enough to sustain AOM, and linked carbonate precipitation to distinctive post-glacial ocean chemistry. However, this view was subsequently challenged by Bristow *et al.* (2011) [153], who argued for a hydrothermal origin, supported by elevated formation temperatures inferred from carbonate clumped isotope thermometry and the presence of coexisting clay minerals suggestive of a thermal alteration history. To resolve this debate, Peng *et al.* (2022) [154] applied an integrated multi-isotope approach including $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{17}\text{O}$ measurements in carbonates, CAS, pyrite, and associated organic matter to reassess the origin of these cements. Their results strongly support a sulfate-driven AOM interpretation, as evidenced by extreme ^{13}C depletion, large ranges in $\delta^{34}\text{S}$, systematic correlations involving negative $\Delta^{33}\text{S}$ values, and consistently low $\delta^{18}\text{O}_{\text{CAS}}/\delta^{34}\text{S}_{\text{CAS}}$ slopes (< 0.4), characteristic of methane-fueled sulfate reduction. These signatures indicate transient post-glacial sulfate maxima, potentially exceeding modern seawater concentrations, developing within ~ 50 kyr of deglaciation, likely driven by intensified oxidative weathering of freshly exposed continental surfaces. The apparent scarcity of comparable signals elsewhere in the Proterozoic underscores the uniqueness of this post-Marinoan interval, highlighting it as a singular geochemical episode rather than a persistent background state.

APPLICATIONS IN CLUMPED ISOTOPES OF CAS

Clumped isotopes in sulfate refer to isotopologues containing two or more rare or heavy isotopes, including ^{34}S , ^{33}S , ^{36}S , ^{18}O , and ^{17}O within a single sulfate molecule. Ueno *et al.* (2021) [155] provided the first experimental determination of ^{34}S – ^{18}O clumping in sulfate by employing partial fluorination of barite at 280°C with excess F_2 or BrF_5 , producing SO_2F_2 while preserving original S–O bonds. Using this approach, Ueno *et al.* documented $\Delta^{34}\text{S}^{18}\text{O}$ values in riverine sulfate as high as $+4.5\text{‰}$ relative to seawater sulfate (defined as 0‰), whereas hydrothermal sulfate from hot springs exhibited negative values (approximately -1.0‰ to -0.5‰). These results demonstrate that $\Delta^{34}\text{S}^{18}\text{O}$ carries information on sulfate provenance, pyrite oxidation pathways, microbial sulfate reduction and recycling fluxes, and high-temperature isotopic equilibration.

Although $\Delta^{34}\text{S}^{18}\text{O}$ measurements have not yet been reported for CAS, this parameter holds considerable promise for paleoenvironmental reconstruction. As analytical precision and methodological frameworks continue to advance, $\Delta^{34}\text{S}^{18}\text{O}$ is likely to emerge as a routine tracer, offering new perspectives on the coupled

evolution of Earth's biosphere and geosphere. At present, however, both the theoretical treatment and analytical application of sulfate clumped isotopes remain at an early, exploratory stage.

SUMMARY AND PROSPECTS

Advancements in CAS geochemistry have transformed our understanding of Earth's oxygenation history, evolving from isolated data points to comprehensive chemostratigraphic timelines, from reliance on single proxies to integrated multi-isotope frameworks, and from qualitative interpretations to rigorous quantitative modeling. By combining CAS high dimensional isotope data with complementary redox proxies—such as redox-sensitive element content and isotopes (e.g., Cr, Mo, V, U, etc.), iron (Fe) speciation, and I/(Ca+Mg) ratios—we can address fundamental questions about Earth's habitability: (1) What triggered the onset of major oxidation events, including the Great Oxidation Event (GOE, ~2.4 Ga), Mid-Proterozoic Oxygenation (MOE, ~1.4 Ga), Neoproterozoic Oxygenation Event (NOE, ~0.8–0.54 Ga), and Paleozoic Oxygenation Event (POE, ~0.45–0.4 Ga)? (2) What were the primary mechanisms driving long-term fluctuations in environmental O₂, such as nutrient (e.g., phosphorus) limitation or enhanced organic burial? (3) How did atmospheric and oceanic O₂ co-evolve spatially and temporally, exhibiting long-term positive feedbacks (e.g., coupled rises) alongside short-term negative feedbacks (e.g., episodic drawdowns during carbon excursions)? (4) What threshold environmental O₂ concentrations were necessary to support the evolution of animal life, from eukaryotic diversification to the Cambrian Explosion? (5) What are the control factors and coupling relationships of Earth's external spheres (atmosphere, hydrosphere, biosphere) on atmospheric oxygen concentrations? (6) What mechanisms link Earth's internal (e.g., mantle-derived volatiles, tectonics) and external spheres, and how do they regulate atmospheric oxygen levels? Future interdisciplinary research spanning geochemistry, biogeochemical modeling, and paleobiology promises to deepen our insights into how Earth transitioned to a habitable state for complex life.

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Conflict of interest

The author declares no conflict of interest.

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